Anodic behavior of amorphous and nanocrystal alloys during the electrochemical processing

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Abstract. Magnetically soft alloys possessing unique characteristics, which determine corrosive, magnetic and other properties, are used as a construction material in the amorphous structural state. The amorphous alloys have a high hardness and unusual fragility along with unique magnetic properties. Due to this fact, there are some limitations in using these alloys as construction materials, which is related to the problems of their processing. Applying traditional methods of mechanical processing is impossible. Thus, the electro-diamond grinding based on the combined action of anodic dissolving and mechanical cutting by the diamond grains is used for processing the open surfaces, for instance, for grooving in the machine stator made of 5BDSR alloy. However, the use of the electrochemical size processing by the cathode-tool based on localizing the anodic dissolving of the machined material is considered to be perspective for processing geometrically complex cavities or holes with a small diameter. To develop the technology of surface forming in details made of 5BDSR and 82K3HSR alloys, the analysis of their anodic behavior during the electrochemical processing was conducted. The reasons for the anode surface passivation during the electrochemical processing of the investigated alloys were found both in amorphous and in amorpho-nanocrystal structural state in 10% electrolytes $NaNO_3$, Na_2SO_4 and NaCl.

1 Introduction

The appearance of new construction materials possessing the unique physical, mechanical and structural characteristics, which determine corrosive, magnetic, tribological and other properties, create good preconditions for increasing the reliability and durability of details in their using in extreme conditions. Magnetically soft alloys obtained during high-speed cooling of the liquid metal are considered to belong to such materials. The amorphous tape with a thickness of 20 - 30 μm used as the construction material for manufacturing stator magnetic circuits of different type and use is formed by molding the metal flat jet on the fast rotating drum. Papers [1 - 3] show that it by changing the structure and the degree of crystallization of the alloys mentioned. The development of the crystallization processes in amorphous alloys under heating and isothermal endurance forms the domain structure and provides the stabilization of the domain boundaries, which along with the peculiarities of

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the thin alloy structure determines it unique magnetic characteristics. The main materials of this class are iron-based alloys (2NSR, 5BDSR) and cobalt-based alloys (82K3HSR, 84KHSR). Such materials as 2NSR, 82K3HSR and 84KHSR are used as the construction material in the amorphous (after molding) condition and the 5BDSR alloy - in the amorpho-nanocrystal state which is formed as a result of a partial crystallization during annealing in the electric furnace. The investigations [1, 4] prove that the degree of alloy crystallization depends on the annealing temperature. The heating of the 5BDSR alloy at a temperature of 530^0 C for an hour forms crystal grains with a size of approximately 15 nm in 38% of the material volume. It proves the incomplete alloy crystallization and its state must be considered as amorpho-nanocrystal. The measurement of magnetic characteristics of the details made of the 5BDSR alloy showed that the best combination of magnetic properties (low coercive force, high values of the saturation induction and magnetic permeability, a low degree of loop rectangularity in the direct and alternating energy field) is observed after annealing in a relatively wide temperature range (500^0C - 600^0C). At the same time, the formation of the best characteristics of the magnetic properties for 82K3HSR, 84KHSR and 2NSR alloys corresponds to particular temperature values (470^0C, 450^0C and 400^0C, respectively). Insignificant overheating from the optimal temperature value leads to a sharp degradation of the magnetic properties. It defines the use of these alloys as the construction materials mainly in the amorphous (after molding) structural state.

There are limitations in using these alloys as the construction materials, which are connected with the problems of their processing to form certain construction elements in the detail, for example, to groove in stator magnetic circuits. The difficulties in processing are determined by the fact that these materials have a high hardness (to 10 - 12 GPa) and an extreme fragility. The use of the traditional methods of the mechanical processing cannot be possible in this case. A highly effective technology of the electro-diamond grinding for slots in iron of the electric machine stator made of 5BDSR alloy is suggested and implemented in Papers [5, 6]. This technology is based on the joint action of anodic dissolving and the mechanical cutting by diamond grains. However, the electro-diamond grinding is suitable for processing the open surfaces and cannot be used for forming, for instance, holes of small diameter, geometrically-complex cavities, etc. To solve such problems the use of the electrochemical size processing by the cathode-tool based on the localization of the anodic dissolving process of the machined material is considered to be perspective [7, 8].

The paper under consideration is devoted to analyzing the anodic behavior of 5BDSR and 82K3HSR alloys during the electrochemical processing. It is necessary for the further development of the surface forming technology in details made of the materials mentioned.

2 Methods of experimental research

The study of the anodic behavior of alloys produced by the metallurgical plant located in the town of Asha was conducted in two structural states - initial (after molding) and after the thermal processing by the potentio-dynamic method to obtain the polarization dependences of the current density on the anode potential. The polarization investigations were conducted at the experimental installation containing a three-electrode electrochemical cell, the construction of which is presented in Paper [9], the ElinsP-20X potentiostat-galvanostat, a computer to give the test program, register and process the data. The samples of the used materials were cut from the tapes as strips with a width of 10 mm and a length of 20 mm. Sample 1 with a soldered contact wire 2 was placed in the ebonite case 3 and was filled up by the epoxy glue 4 (Figure 1). The potentio-dynamic investigations were accomplished under the potential sweep in the range from 0 V to 12 V

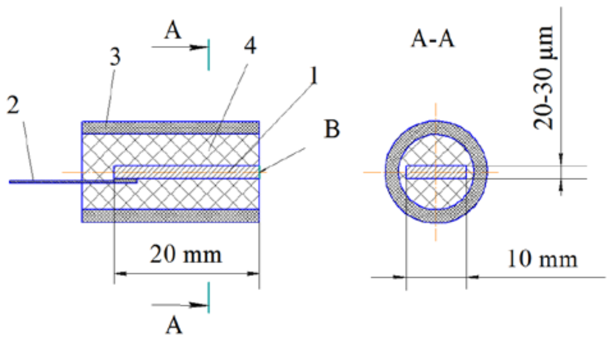

Fig. 1. Case construction with a sample for the polarization investigations.

at a speed of 200 mV/s and a step of 0.582 mV. The value of the inter-electrode gap between the anode surface, which is the sample surface B (Figure 1), and the platinum electrode of comparison was equal to 0.1 mm. After each experiment, the sample surface was cleaned by the abrasive paper of P600 with the grain structure 20-28 µm to remove the traces of electrochemical dissolving.

Ten percent water solutions of the NaCl, $NaNO_3$, Na_2SO_4 neutral salts chosen on the recommendations of Papers [10] were used as electrolytes for electrochemical investigations.

3 Results and discussion

The potentio-dynamic polarization curves of anodic dissolving of the investigated materials in chosen electrolytes are presented in Figures 2 - 7.

The analysis of the polarization test results gives the ground to state that both the stages of the active dissolving when the potential increase is accompanied by the current density growth and the passivation stages, which result in the speed slowdown of anodic dissolving, are typical of both materials during processing in all the electrolytes. More intensive dissolving of the processed material after the thermal processing (curves 2) in comparison with the initial (amorphous) state (curves 1) is common for all the presented dependences. It is proved by the current density increase in the zones with the active dissolving of the materials having the elements of the nanocrystal structure formed during the thermal processing. The fact mentioned is obvious because the appearance of defects as boundaries during the crystallization promotes to intensifying the corrosion processes. The presence of the passivation areas on the polarization curves in a certain range of potentials is explained by the formation of non-soluble oxide films (layers) on the anode surface and by oxygen absorption on it. In this case, the absorption of oxygen occurs at lower potential values in comparison with the equilibrium potential of oxide formation. Absorption and oxide films either partially slow down the process of anodic dissolving (Figures 3, 4) or result in a sharp reduction of the current density with the potential growth (Figures 2, 5, 6). It should be noted that while processing the alloys in $NaNO_3$ and Na_2SO_4, the zone of active dissolving starts in achieving the potential value 2 V (Figures 2, 3, 5, 6). Another character of anodic behavior in the zone of active dissolving is seen in using the solution of sodium chloride (Figures 4, 7). The introduction of the chlorine anions in the solution, which are activating, shifts the beginning of active dissolving in the zone of lower potential values. It is connected with the fact that the chlorine anions in part or in whole displace oxygen from

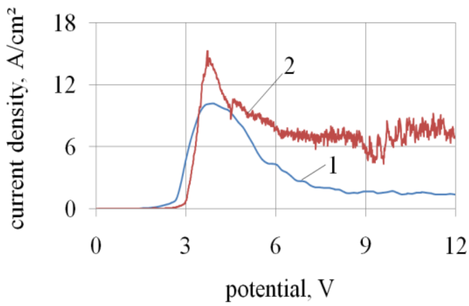

Fig. 2. Potentio-dynamic polarization curves of the 5BDSR alloy anodic dissolving in 10% $NaNO_3$: 1 – before the thermal processing; 2 – after the thermal processing

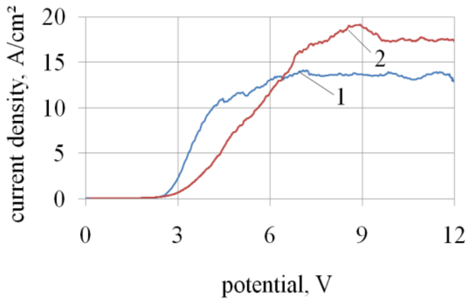

Fig. 3. Potentio-dynamic polarization curves of the 5BDSR alloy anodic dissolving in 10% Na_2SO_4: 1 – before the thermal processing; 2 – after the thermal processing

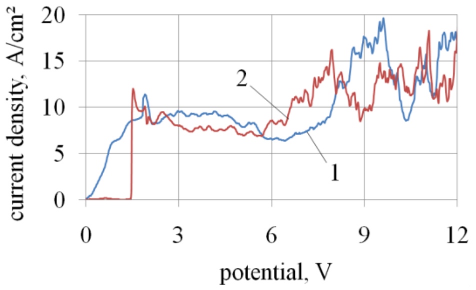

Fig. 4. Potentio-dynamic polarization curves of the 5BDSR alloy anodic dissolving in 10% NaCl: 1 – before the thermal processing; 2 – after the thermal processing

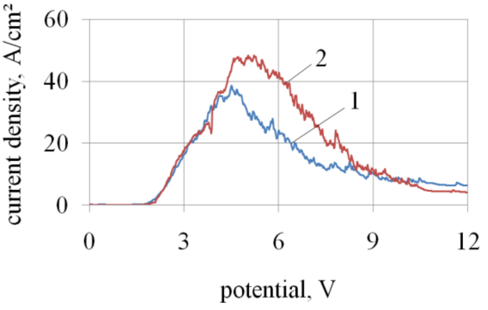

Fig. 5. Potentio-dynamic polarization curves of the 82K3HSR alloy anodic dissolving in 10% $NaNO_3$: 1 – before the thermal processing; 2 – after the thermal processing

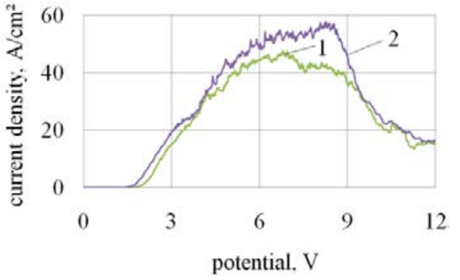

Fig. 6. Potentio-dynamic polarization curves of the 82K3HSR alloy anodic dissolving in 10% Na_2SO_4: 1 – before the thermal processing; 2 – after the thermal processing

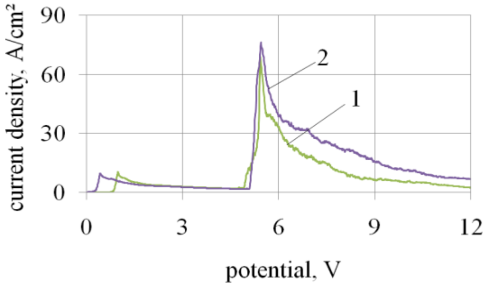

Fig. 7. Potentio-dynamic polarization curves of the 82K3HSR alloy anodic dissolving in 10% NaCl: 1 – before the thermal processing; 2 – after the thermal processing

the passivating oxide films on the anode surface, forming the compound with the metal, for example, $FeCl_2$ in processing the 5BDSR alloy (Figure 4). This compound is easily dissociated in the electrolyte solution.

The polarization curve of anodic dissolving the 82K3HSR amorphous alloy in the sodium chloride solution has somewhat different character (Figure 7). After a small zone of active dissolving in a narrow range of potentials (0.5 V – 1.0 V), the material changes into the passive state with a significant reduction in the current density up to the potential value of 5 V. Such behavior is explained by the presence of chrome in the composition of the 82K3HSR amorphous alloy. It is known [11] that the introduction of more than 13% (at.) of chrome in crystal metals turns them into the corrosion-resistant steels. It is related to the fact that there is no accumulation of chrome in the surface film in its less concentration in crystalline alloys during the passivation. The film mainly consists of the hydrated oxide – the copper hydroxide, which is considerably inferior in its anticorrosive properties to the passivating film from the hydrated chrome oxide-hydroxide. Unlike crystalline alloys, the chrome content in the amorphous alloy equal to 3% (at.) increases its amount in the passivating film by more than 50%. The presence of the activating chlorine anions in the solution, which act as a catalyst, results in substituting oxygen in the oxide film, thus forming the $CrCl_2$ compound, easily dissolved in water. As a result of the anode surface depassivation, a sharp rise in the current density is observed at a potential value of 5 V, which characterizes active dissolving of the amorphous alloy. Then the zone of active dissolving is again changed by the passivation zone. At the same time the authors [11] consider that the main mechanism of the anode surface depassivation is the destructive action of the gaseous chlorine on the passivating film.

4 Conclusions

It is established experimentally that electrochemical dissolving of the 5BDSR and 82K3HSR alloys in the initial and annealed states in the water solutions of the neutral salts is accompanied by the passivation processes connected with forming absorption and oxide films on the processed surfaces. Forming the detail surfaces made of the materials of this class by using electrochemical processing will require a search for solutions to removing the passivation phenomena. The use of the existing mechanisms for activating the electrochemical processing (heat, hydraulic, light-hydraulic, photo-activation, etc.) separately or in a certain combination will be determined by the possibility of their implementing in the processes of forming.

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